Letters to the Editor

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ASYMMETRICAL RAMAN SCATTERING BY WATER AND SULPHURIC ACID

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Sokolovskaya and Simova (1963) observed, recently, that in the cases of C_6H_6, $C_6H_5CH_3$, CS_2 and CCl_4, the intensity of the Raman lines asymmetrical, i.e., scattering at an angle θ is different from what it is at $180-\theta$. This is surprising as Raman scattering is generally considered to be incoherent. A similar observation had been reported much earlier by Pokorowski and Gordon (1930) in the case of water.

Rank (1948) observed another type of asymmetry in the case of CCl_4, $CHCl_3$, C_6H_6 and CS_2. Now, if light is polarised with its electric vector along the axis of the Raman tube (H) is incident on the sample tube and the scattered light analysed, the component in the plane of observation and incidence (H_h) and the one perpendicular to it (H_v) are generally considered to be equal if one considers

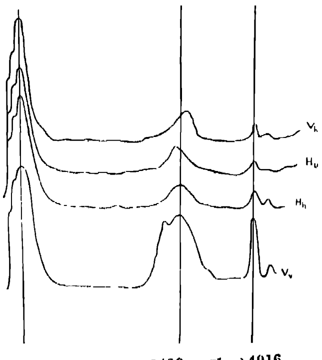

Fig. 1. Microphotometric traces of Raman spectra of water showing the four polarised components.

that Raman scattering is incoherent. Rank observed that in the above cases $H_h \neq H_v$.

If incident light is polarised in the vertical plane (V i.e. perpendicular to the plane containing the directions of incidence and observation) and the scattered light analysed one gets V_v and V_h Krishnan (1934) has shown that even in the case of colloidal solutions, for which the Rayleigh scattering is asymmetrical, $H_v = V_h$ This is called the reciprocity relation.

Now, we report that for the water band at 3400 cm^{-1} and the Raman lines $d\nu = 410$ and 560 of sulphuric acid, the differently polarised components

show that all the precautions are taken to guard against experimental errors and that the above results are not due to any such errors. A fuller description will be published elsewhere in connection with some other results.

Now, to show that $H_h \neq H_v \neq V_h$, for any particular Raman line,, very stringent precautions should be taken, and preferably, photo-electric recording should be resorted to But, in the case of $d\nu = 3400$ of water, the matter is much simplified. It really consists of two components at about 3200 and 3400, the former being weaker According to the present simple theory of Raman scattering by liquids, the three polarisation components should be equal for both the parts 3200 and 3400. Hence, the structure of the composite band should retain its shape in all the three spectra The structural differences demonstrated in the fig 1 can only be due to the fact that either one of them or both must be violating this requirement. It is very difficult to think of any experimental error that can bring about this differential behaviour of the two parts of the band. Similarly, $d\nu = 410$ and 560 of sulphuric acid are also of composite nature, the former due to the splitting of a doubly degenerate line and later due to a triply degenerate mode. Differential behaviour of these lines in the two spectra is seen more conspicuously than in the case of water.

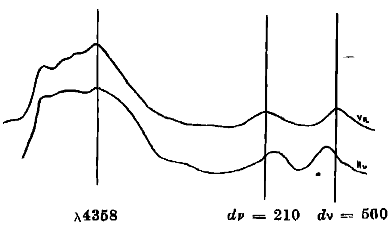

Fig Microphotometric traces of Raman spectra of H_2SO_4 showing structural differences between V_h and H_v.

It may be mentioned in this connection, that $d\nu = 3400$ of water as excited by $\lambda 4046$ is used in this investigation. On this is superposed a very weak band of frequency about 1600 cm^{-1} which is excited by $\lambda 4358$. Its intensity is of the order of 5% of $d\nu = 3400$ This does not bring about the structural changes observed as this band also should follow the law that the three differential polarised components are equal. In this investigation a filter with iodine in CCl_4 is used to reduce the intensity of $\lambda 4358$ to about 1/3

EXPERIMENTAL

Light is allowed to pass through a system of parallel vanes 1 mm apart and one inch long and be incident on a polaroid strip cut in the proper way to allow either V or H components. Light, thus rendered parallel and polarised is incident on the Raman tube. Scattered light is analysed by a split polaroid kept almost touching the slit of the spectrograph, so that one part transmits h and the other the v component. The pair of photographs V_v and V_h and H_v and H_h are thus

g 3. Raman Spectrum of CCl_4 with incident light H polarised, to demonstrate the absence of $d = 459$ which is very sensitive to convergence, leak of the polaroid in the incident light, extraneous light etc

exposed simultaneously. To eliminate error due to differential transmission of the spectrograph, the arrangement, including the split polaroid is rotated by 45° so that, light is incident on the sample at an angle of 45° to the horizontal plane A spectrum of CCl_4 taken under these conditions and showing H_h and H_v components shows that $d\nu = 459$ is almost absent (fig. 3) It is about 1% as intense as $d\nu = 313$ while these two are of equal intensity in a spectrum taken with incident light unpolrised. It will show itself prominently, if the arrangment is defective by way of (1) convergence of the incident light (2) convergence of the scattered light (3) leak of the polariod in the incident light and (4) extraneous light (of unpolarised nature) falling on the sample tube. $d\nu = 217$ and 313 appear identical in H_h and H_v showing the absence of (1) differential transmission of the spectrograph for v and h components and (2) polarisation of scattered light by reflection on the walls of the sample tube

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